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ATTORNEY'S DOCKET NUMBER

GRIHAC P28AUS

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (Of course, use 37 CFR 1.5)

09/463423

INTERNATIONAL APPLICATION NO.
PCT/AU98/00576

INTERNATIONAL FILING DATE

22 July 1998

PRIORITY DATE CLAIMED

23 July 1997

TITLE OF INVENTION

PHOTO-ASSISTED OXIDATION OF INORGANIC SPECIES IN AQUEOUS SOLUTIONS/

APPLICANT(S) FOR DO/EO/US

Ging Hauw KHOE, Myint ZAW, Patricia Salini PRASAD and Maree Therese EMETT.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau. (PCT/IB/308 mailed 04 February 1999).
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)) is attached.
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98 with PTO FORM 1449.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
 - ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

<input checked="" type="checkbox"/> Preliminary Examination Report <input checked="" type="checkbox"/> Annexes to Pre. Ex. Rep. <input checked="" type="checkbox"/> International Search Report <input type="checkbox"/> German Novelty Search Report <input type="checkbox"/> ___ copies of citations <input type="checkbox"/> Form PCT/IB/308 <input checked="" type="checkbox"/> International Publ. No. WO 99/05065 (Face page only)	<input type="checkbox"/> Copy of Request <input checked="" type="checkbox"/> 10 sheets of formal drawings <input type="checkbox"/> Abstract <input type="checkbox"/> Verified Statement Claiming Small Entity Status <input checked="" type="checkbox"/> Submission of Incomplete Application <input type="checkbox"/> German Language Specification
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CERTIFICATION UNDER 37 CFR 1.10

I hereby certify that this Transmittal Letter and the papers indicated as being transmitted therewith is being deposited with the United States Postal Service on this date **January 21, 2000** in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number **EL347242759US** addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Michael J. Bujoel

(typed or printed name of person mailing paper)

(signature of person mailing paper)

514 Rec'd PCT/PTO 21 JAN 2000

17. The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search Report has been prepared by the EPO or JPO \$840.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) \$670.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$970.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT = 970

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)). 0

Claims	Number Filed	Number Extra	Rate		
Total Claims	620 =	0	x \$18.00	0	
Independent Claims	1-3 =	0	x \$78.00	0	
Multiple dependent claim(s) (if applicable)			+ \$260.00	0	

TOTAL OF ABOVE CALCULATIONS = 0

Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28). 0

SUBTOTAL = 970

Processing fee of \$130.00 for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). + 0

TOTAL NATIONAL FEE = 0

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + 0

TOTAL FEES ENCLOSED = 970

Amount to be:
refunded \$
charged \$

a. ☒ A check in the amount of \$ 970.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. 04-0213 in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 04-0213. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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01/21/0

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of : Ging Hauw KHOE, Myint ZAW, Patricia Salini
Serial no. : PRASAD and Maree Therese EMETT
For : PHOTO-ASSISTED OXIDATION OF INORGANIC
SPECIES IN AQUEOUS SOLUTIONS
Docket : GRIHAC P28AUS

BOX PCT

The Commissioner of Patents and Trademarks
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

By way of preliminary amendment, please amend the above identified application as set forth below.

In the Claims:

Please cancel original claims 1-9, without prejudice or disclaimer of the subject matter therein, in favor of new claims 10-17 as follows.

10. A method for oxidizing an inorganic species in an aqueous solution comprising the steps of:

- (i) supplying an oxidizable source of sulphur, and oxygen to the solution; and
- (ii) irradiating the solution with UV light such that the species is oxidized.

11. The method as claimed in claim 10, wherein the oxidizable source of sulphur is SO_3^{2-} , $\text{SO}_2(\text{g})$, aqueous SO_2 , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$.

12. The method as claimed in claim 10, wherein the inorganic species is present in the aqueous solution in trace quantities.

13. The method as claimed in claim 10, wherein the inorganic species is arsenic, manganese, cerium, and/or iron.

14. The method as claimed in claim 10, wherein the wavelength of UV light is less than 300 nm.

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15. The method as claimed in claim 10, wherein dissolved oxygen is derived from air.

16. The method as claimed in claim 10, wherein dissolved oxygen is derived from a gas source with an oxygen partial pressure of about 0.2 atmospheres.

17. The method as claimed in claim 10, wherein the aqueous solution is one of: drinking water, industrial waste water, or an industrial process liquor.

REMARKS

Please enter the above before consideration of this application.

In the event that there are any fee deficiencies or additional fees are payable, please charge the same or credit any overpayment to our Deposit Account (Account No. 04-0213).

Respectfully submitted,



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PHOTO-ASSISTED OXIDATION OF INORGANIC SPECIES IN
AQUEOUS SOLUTIONS

Abstract of the Disclosure

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A method for oxidizing an inorganic species in an aqueous solution comprises the steps of: (i) supplying an oxidizable source of sulphur, and oxygen to the solution; and (ii) irradiating the solution with UV light such that both the inorganic and sulphur species are oxidized.

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PHOTO-ASSISTED OXIDATION OF INORGANIC SPECIES
IN AQUEOUS SOLUTIONS

Field of the Invention

5 The present invention relates to a method for
oxidising inorganic species in aqueous solutions, and more
particularly, to the treating of contaminants in e.g. human
drinking water, and industrial waste waters and process
liquors. However, it should be appreciated that the
10 invention can be employed wherever it is necessary to
oxidise an inorganic species in aqueous solutions for
whatever reason.

Background to the Invention

 Dissolved sulphur dioxide or sulphite is usually
15 considered to be a reducing agent. Further, it is known
that the oxidation of sulphite is accelerated through
exposure to UV radiation (Matthews, J.H. et.al.
J.Am.Chem.Soc.1917,39, 635). Matthews teaches, however,
that oxidation is retarded by the presence of trace amounts
20 of various species. In addition, no change in the
oxidation state of these species was observed.

 Many drinking water supplies across the world are
contaminated by trace contaminants including arsenic, iron
and manganese. World Health Organisation standards require
25 very low levels of contaminants (for example arsenic-a 10
ppb limit). The presence of manganese gives rise to "dirty
water" problems and can result in soiling of clothes and
staining of household fixtures when present in
concentrations in excess of 20 ppb in drinking water.

30 Many waste waters and mineral processing liquors from
industry also include arsenic, iron, manganese and cerium,
and in the field of nuclear technology, uranium.

 As part of the removal process, chemical oxidants such
as chlorine, ozone and permanganate are often used.

35 However, these oxidants can give rise to harmful byproducts

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such as chloroform, and the presence of residual permanganate can produce discoloured waters.

Summary of the Invention

The present invention provides a method for oxidising an inorganic species in an aqueous solution comprising the steps of:

- (i) supplying an oxidisable source of sulphur, and oxygen to the solution; and
- (ii) irradiating the solution with UV light such that the species is oxidised.

In the present invention, oxygen is advantageously used as the oxidising agent, with no residual contaminating after-effects. Sulphur sources can be selected, (e.g. sulphite) such that in the oxidising procedure, a relatively benign product is produced (e.g. sulphate). Although the final product of using sulphite is a relatively benign dissolved sulphate, it is preferable to use it sparingly especially if an ion-exchange process is subsequently used to remove the contaminant (e.g. arsenic). In this case dissolved sulphate of no more than 25 mg/L is preferred in order to obtain effective arsenic(V) removal (sulphate and arsenate compete for sites on the ion-exchange material).

The oxidisable sources of sulphur can be SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{SO}_2(\text{g})$, aqueous SO_2 , or HSO_3^- . However, sulphur dioxide and sulphite are preferred sources.

Typically the process is applied in the treatment of trace quantities of inorganic species but the process can also find application with more concentrated quantities of contaminants.

Typically the species oxidised includes one or more of arsenic, manganese, cerium and/or iron.

Typically the ultraviolet light employed has a wavelength of about 254nm. Radiation can be supplied continuously or in pulses. Furthermore, low, medium or high pressure mercury arc lamps can be used as the source

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of the UV radiation. It was also noted that UV wavelengths of 254nm from a lamp source advantageously disinfected water so treated.

Typically the oxygen is sparged into the aqueous solution as air but other methods of addition are possible. As indicated above, the solution is typically a drinking water solution, an industrial waste water or process liquor etc.

Typically the pH of the solution is, if necessary, adjusted to be approximately neutral or basic.

Brief Description of the Drawings

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings and the following non-limiting examples. In the drawings:

Figure 1 is a graph that plots the increase in arsenic(V)-concentration and concomitant decrease in sulfite-concentration as a function of illumination time using a 15 W low-pressure mercury lamp. The corresponding change in arsenic(V) concentration in darkness is also shown. (Initial conditions: 1.7 litre of solution containing 470 ppb arsenic(III) in the presence of 10 mg/L sulfite, solution pH adjusted to 9 using sodium carbonate).

Figure 2 is a graph that plots the increase in arsenic(V) concentrations as a function of illumination time using a 15 W 254 nm lamp. (Initial conditions: 1.7 litre of solution containing arsenic(III) concentration of approximately 470 ppb, pH adjusted to 9 using sodium carbonate, initial sulfite concentrations varied from 0 to 12 mg/L).

Figure 3 is a graph that plots arsenic(V) concentrations as a function of elapsed time when solutions (1.7L) containing arsenic(III) at a concentration of 470 ppb, at various controlled pHs, were illuminated with a 15 W 254 nm lamp. Sodium sulphite solution was added at a

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dose rate of 2 mg/L/min and air was sparged at a rate of 2.5 L/min. Data with no UV illumination (dark) are also shown.

Figure 4 is a graph that plots arsenic(V) concentrations as a function of elapsed time when a solution (1.7L) containing arsenic(III) at a concentration of about 20 mg/L, at pH 6.5, was illuminated with a 15 W 254 nm lamp. Sulphur dioxide gas was injected at a rate of about 0.02 L/min and air was sparged at a rate of 2.5 L/min. Data with no UV illumination (dark) are also shown.

Figure 5 is a graph that plots arsenic(V) concentrations as a function of elapsed time when solutions (1.7L) containing arsenic(III) concentration of 470 ppb, at pH 6.5, were illuminated with a 15 W 254 nm lamp. Sodium thio-sulphate solution was added at various dose rates (in mg/L/min) and air was sparged at a rate of 2.5 L/min. Data with no UV illumination (dark) are also shown.

Figure 6 is a graph that plots arsenic(V) concentrations as a function of elapsed time when a solution (1.7L) containing arsenic(III) at a concentration of 470 ppb, at pH 6.5, was illuminated with a 15 W 254 nm lamp. Sodium tetra-thionate solution was added at a dose rate of 2 mg/L/min and air was sparged at a rate of 2.5 L/min. Data with no UV illumination (dark) are also shown.

Figure 7 is a graph that plots residual manganese concentrations as a function of elapsed time when solutions (1.7L) containing manganese(II) concentration of about 500 ppb, at pH 8.5, were illuminated with a 15 W 254 nm lamp. Sodium sulphite solution was added at a dose rate of 2 mg/L/min and air was sparged at a rate of 2.5 L/min. The oxidised manganese was removed using a 0.025 micron membrane filter. To facilitate manganese removal, ferric chloride (6.2 mg Fe/L) was added in 2 of the 4 tests. Data with no UV illumination (dark) are also shown.

Figure 8 is a graph that plots residual manganese concentrations as a function of elapsed time when a

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5 solution (1.7L) containing manganese(II) at a concentration of about 20 mg/L, at pH 9.5, was illuminated with a 15 W 254 nm lamp. Sodium sulphite solution was added at a dose rate of 80 mg/L/min and air was sparged at a rate of 2.5 L/min. Ferric chloride was added at 6.2 mg Fe/L to facilitate the manganese removal. Data with no UV illumination (dark) are also shown.

10 Figure 9 is a graph that plots iron(II) concentrations as a function of elapsed time when a solution (1.7L) containing iron(II) at a concentration of about 20 mg/L, at pH 2, was illuminated with a 15 W 254 nm lamp. Sodium sulphite solution was added at a dose rate of 20 mg/L/min, air was sparged at a rate of 2.5 L/min. Data with UV without sulphite, and no UV illumination (dark) are also shown.

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20 Figure 10 is a graph that plots cerium(IV) concentrations as a function of elapsed time when a solution (1.7L) containing cerium(III) at a concentration of 20 mg/L, at pH 6.5, was illuminated with a 15 W 254 nm lamp. Sodium sulphite solution was added at a dose rate of 20 mg/L/min, air was sparged at a rate of 2.5 L/min. Data with UV illumination but without sulphite, and no UV illumination (dark) are also shown.

Modes for Carrying Out the Invention

25 Preferred forms of the present invention find application in the treatment of drinking water, waste waters and mineral processing liquors. It should be appreciated, however, that the invention has broader applications.

30 With drinking water treatment, it is desirable to remove trace oxidisable contaminants, such as arsenic and manganese. In at least preferred forms, contaminants are oxidised and then removed under neutral or slightly alkaline conditions.

35 In the treatment of waste waters and mineral processing liquors, it is desirable to neutralise and/or

remove (depending on the final use of the water or liquor) species such as arsenic, iron and manganese. In these applications, however, oxidation may take place in acid, neutral or alkaline conditions.

5 Manganese-related "dirty water" problems are a significant water quality issue to water supply authorities. It is understood that 40 per cent of public water supplies in the United States have manganese concentrations exceeding levels of 10-20ppb.

10 Manganese is also a problem in processed wastes in the milling of uranium ores and in acid mine drainage. Manganese is often present in the ore to be milled, and may be also introduced as an oxidant in the form of a pyrolusite (MnO_2) which is an oxidant used in the leaching
15 of uranium.

In industrial process liquors, it is necessary to oxidise various metal ions as part of the overall processing in the plant.

20 Details of various preferred process operating parameters are now described.

Source of Radiant Energy

Any source of radiant energy in the UV region of the electromagnetic spectrum was observed to be useful, provided that the radiation was absorbed by the dissolved
25 sulphur compound which was acting as the photo-initiator of the process. Low pressure mercury arc lamps were used for the oxidation of dissolved arsenic(III), manganese(II), iron(II) and cerium(III). Typical UV wavelengths of less than 300nm were employed (preferably about 254nm).

30 Choice of Photo-Absorber

Dissolved sulphur species absorbed the supplied UV light and were oxidised by dissolved oxygen. These sulphur species were used up (oxidised) during the photochemical reaction. Dissolved sulphur(IV) species derived from the
35 addition of sodium sulphite included SO_3^{2-} , HSO_3^- or H_2SO_3 depending on the pH value of the solution. The same

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dissolved sulphur species were obtained by dissolving SO_2 gas in water which gives aqueous SO_2 which, in turn, converted to sulphurous acid (H_2SO_3). Sulphurous acid dissociated to HSO_3^- and SO_3^{2-} at higher pH conditions.

- 5 Dissolved sulphite from sodium sulphite was used for the oxidation of manganese(II).

Other partially oxidised sulphur species (sulphur(VI) as in sulphate compounds having fully oxidised sulphur species) obtained from the dissolution of sodium
10 thiosulphate or sodium tetrathionate were also used as the photo-absorber.

Furthermore, dissolved sulphite was obtained by sparging sulphur dioxide gas or a gas mixture of sulphur dioxide and air/oxygen/nitrogen into the solution. Thus,
15 the forms of sulphur employable included SO_3^{2-} , $\text{SO}_2(\text{g})$, aqueous SO_2 , HSO_3^- , $\text{S}_2\text{O}_3^{2-}$ and $\text{S}_4\text{O}_6^{2-}$.

Source of Oxidant

Oxygen was the oxidant for the photochemical oxidation process. It was typically supplied at about 0.2
20 atmospheres partial pressure by aerating the reaction mixture. Alternatively, oxygen was supplied by sparging a gas mixture of sulphur dioxide with air, or an oxygen/nitrogen mixture into the solution (or any other compatible gas source). Oxygen partial pressures greater
25 than or less than 0.2 atm can also be used as appropriate.

Illumination was achieved by placing a lamp within a quartz envelope inside the reaction vessel (alternatively, the light can be directed from above the solution). Types of lamp used included a high or low pressure mercury arc
30 lamp or a xenon arc lamp.

It was noted that where the UV source chosen emitted light at a wavelength at about or below 190 nm, ozone was generated from the dissolved oxygen; (ozone is a powerful oxidant which can oxidise arsenic(III) and manganese(II)).
35 For the examples described below, non-ozone producing lamps were employed.

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Examples

Non-limiting examples will now be described.

Photo-Oxidation of Dissolved Arsenic(III)

- A reaction mixture (1700 mL) containing 470 µg/L As(III) (typical concentrations in ground water in areas where arsenic is leached from the naturally occurring arsenic-containing minerals) and 10 mg/L of dissolved sulphite (SO_3^{2-}) was prepared as follows: the sulphite stock solution was prepared by dissolving sodium sulphite salt in demineralised water; the arsenious acid (As(III)) solution was obtained by dissolving arsenic trioxide in warm, demineralised water. The pH of the reaction mixture was adjusted to 9 with the addition of sodium carbonate (because groundwaters typically have significant carbonate alkalinity). The solution was then aerated by the injection of fine bubbles of air.

- In the absence of UV illumination, no significant oxidation of As(III) was observed (Figure 1). When a 15 W low pressure mercury lamp was switched on to illuminate the reaction mixture, the oxidation of As(III) and S(IV) proceeded rapidly (Figure 1).

- The experiments were repeated using various initial concentrations of dissolved sulphite, namely from 0 to 12 mg/L of dissolved sulphite. As shown in Figure 2, the rate of As(III) oxidation was strongly dependent on the initial sulphite concentration when it was less than 8 mg/L. Figures 1 and 2 demonstrate that both UV light and dissolved sulphite were needed for the photo-oxidation reaction to occur.

- Figure 3 shows that the arsenic oxidation rate was increased by the increase in the solution pH. During these test runs, the solution pH was controlled at the selected value using an automatic titrator which added sodium hydroxide solution when required. Sodium sulphite was added by the continuous injection of a stock solution (17 g/L of sulphite) at a precisely controlled flow rate using

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5 a titrator in order to give a dose rate of 2 mg/L i.e. 0.2 mL/min of the stock solution was injected into the 1.7 L of reaction mixture. This method of sulphite dosing is more efficient than the procedure described for Figures 1 and 2 where the sodium sulphite was added in a single dose. It also simulates the procedure where SO₂ gas is used. Air was sparged at a rate of 2.5 L/min.

10 Sulphur dioxide gas was used instead of sodium sulphite as shown in Figure 4. Arsenic(III) was oxidised when sulphur dioxide and air was bubbled in the absence of UV illumination (auto oxidation process). However, the oxidation rate was accelerated when the reaction mixture was illuminated. It was observed that significant concentrations of dissolved sulphite were present in the
15 reaction mixture indicating that an excess sulphur dioxide was sparged. Hence, the difference between the results of the 'light' and 'dark' experiments was not large as could be achieved.

20 Sodium thiosulphate can be substituted for sodium sulphite as shown in Figure 5. Similarly, sodium tetrathionate was used as the photo-absorber as demonstrated in Figure 6.

Actinometry determination using potassium ferrioxalate showed that a maximum of 6 Watts of 254 nm radiation
25 produced by the 15 W lamp was absorbed by the reaction mixture. Total As and As(III) concentrations were determined using atomic absorption spectroscopy with hydride generation. Concentrations of As(V) in the reaction mixture were determined using the molybdenum blue
30 spectrophotometric method (Johnson D. and Pilson M., Analytical Chimica Acta, 58, 289-299 (1972)). Sulphite concentrations were also determined spectrophotometrically (Humphrey R.E., Ward M.H. and Hinze W., Analytical Chemistry, 42, 698-702 (1970)).

Photo-Oxidation of Dissolved Manganese(II)

A reaction mixture (1700 mL) containing 500 µg/L Mn(II) (typical concentrations in surface and ground water are less than 1 mg/L) and 10 mg/L SO_3^{2-} , was prepared as follows: the sulphite stock solution was prepared by dissolving sodium sulphite salt in demineralised water; the Mn(II) stock solution was obtained by dissolving $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in demineralised water. The pH of the reaction mixture was 6.5 and it was aerated by the injection of fine bubbles of air.

After a 15 W low pressure mercury lamp was switched on to illuminate the reaction mixture for 2 minutes, the reaction mixture became cloudy because of the appearance of grey/black suspended particles indicating that an oxide of manganese had been formed. A 25 mL sample was collected and its pH (4 - 5) was adjusted to 7 using dilute sodium hydroxide solution in order to coagulate colloidal manganese oxide particles. After 30 minutes, to allow the precipitated grey/black particles sufficient time to coagulate, the sample was filtered using an Amicon unit fitted with 0.025 µm membrane. The dissolved Mn concentration in the filtrate was 22 µg/L. This indicates that most of the dissolved Mn(II) was oxidised to Mn(III)/Mn(IV) and precipitated as manganese oxide (which is black).

When the same procedures were repeated without illumination, the reaction mixture remained clear and colourless. A sample was taken after 30 minutes and subjected to the coagulation and filtration procedure. The manganese concentration in the filtrate was 505ppb (Table 1).

Dissolved manganese concentrations were analysed using ICP-MS, ICP-AES or atomic absorption spectroscopy with a graphite furnace.

The results of one SUCH procedure are summarised in

Table 1.

Table 1

Residual manganese concentration in water after filtration.
Concentration in parts per billion

5

Initial Concentration	511 ppb
After 2 min illumination at pH 6.5 in the presence of 10 mg/L sulfite	22 ppb
After 30 minutes without illumination	505 ppb

Photo-Oxidation of Other Dissolved Compounds

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The above procedures can also be employed with the photo-oxidation of dissolved compounds such as Se(IV), CN⁻, Fe(II), Ni(II), V(IV), U(IV), and Ce(III). Oxidation can be demonstrated by making up a reaction mixture containing an appropriate concentration of one or more of these compounds. Dissolved sulphur species can be obtained from stock solution which can be prepared by dissolving either the equivalent sodium or calcium salt in water. The mixture can then be divided into three portions for a set of three tests:

1. No UV illumination. To the first portion of the reaction mixture, an appropriate amount of sulphite or sulphide is added from a concentrated stock solution. The mixture is aerated with a nitrogen-oxygen mixture of known oxygen partial pressure. Speciation of the oxidation state of the target substance and the sulphur at several time intervals was used to determine the reaction rate.
2. The second portion of the reaction mixture is aerated with the same oxygen/nitrogen gas mixture used in Test 1 and illuminated without the addition of a sulphur compound.

3. The final portion is aerated with the same addition of sulphite or sulphide as used in Test 1 and the light was then turned on to start the experiment. The oxidation rate is determined as above for As(III) and Mn(II).

Illumination can be achieved by placing a lamp either within an envelope inside the reaction vessel or such that the light radiates from above. Types of lamps used can include a high or low pressure mercury arc lamp, a Xenon arc lamp or a blacklight blue fluorescent tube.

It would be observed that the rate of oxidation of the target substance in Test 3 is greater than that in either Tests 1 or 2.

Procedure for Experiments Using Sulphur Dioxide Gas

The photo-oxidation reaction can proceed just as well when sulphur dioxide gas is used instead of sulphite salt. In order to demonstrate this, for each target substance, a set of three tests can be performed as in the previous section. The reaction mixture can be sparged with a fine stream of gas bubbles. The partial pressure of oxygen, sulphur dioxide and nitrogen can be independently varied in the gas stream from 0 to 100%.

Test A Sulphur dioxide is added to the oxygen/nitrogen gas stream at a known partial pressure, in the absence of any illumination, and the rate of oxidation was determined by speciating the oxidation state of the target substance after several time intervals.

Test B The vessel is designed so that the second portion of the reaction mixture was illuminated with light from a lamp, in the absence of sulphur dioxide. The slow background oxidation rate (if any) is determined by speciating the target substance for oxidation state at several time intervals.

Test C The third portion of the reaction mixture is placed in the reaction vessel. Sulphur dioxide was added

to the gas stream and the lamp is switched on at the same time, to mark the beginning of the experiment. The sulphur dioxide partial pressure is the same as that in Test A and the illumination source and lamp intensity were the same as that in Test B.

The rate of oxidation of the target substance in Test C would be greater than that in Tests A or B.

The pH of the reaction mixture and the addition of sodium sulphite solution were controlled using automatic titrators as described above. The oxidation of manganese was evidenced by the appearance of grey/black suspended particles indicating that an insoluble oxide of manganese(III) or (IV) had been formed. Preliminary measurements using electron paramagnetic resonance spectroscopy confirmed that the concentration of dissolved Mn(II) decreased with the elapsed time of illumination.

The precipitated manganese particles were removed using an Amicon unit fitted with 0.025 micron membrane filter. As shown in Figure 7, the addition of ferric chloride solution to give a concentration of about 6 mg Fe/L in the reaction mixture improved the removal of manganese from solution. The residual manganese concentrations were analysed using ICP-MS, ICP-AES or atomic absorption spectroscopy with graphite furnace.

As shown in Figure 7, at pH 8.5, the rate of removal of manganese from solution was accelerated by the illumination of the reaction mixture using UV light from a low-pressure mercury lamp. The oxidation of a more concentrated solution of Mn(II) at pH 9.5 is depicted in Figure 8. Here, the dosing rate of sulphite was increased to 80 mg/L/min to account for the initial Mn(II) concentration of 20 mg/L.

Photo-oxidation of Dissolved Iron(II) in Acid Conditions

The oxidation of iron(II) was followed by periodically measuring the residual dissolved iron(II) concentration in the reaction mixture. This was determined

spectrophotometrically using ferrozine reagent (Stookey, Analytical Chemistry, Vol. 42, No. 7, 1970).

Figure 9 shows iron(II) concentrations as a function of elapsed time when a solution (1.7L) containing iron(II) at a concentration of about 20 mg/L, at pH2, was illuminated with a 15 W 254 nm lamp. Sodium sulphite solution was added at a dose rate of 20 mg/L/min, air was sparged at a rate of 2.5 L/min. The oxidation data with UV illumination but without sulphite indicated that the oxidation of Fe(II) by dissolved oxygen was accelerated by UV illumination. This was due to the fact that dissolved Fe(II), which is a mild photo-absorber of light at 254 nm wavelength, photo-initiated and sustained the oxidation reaction. Dissolved Fe(II) was oxidised in the presence of dissolved sulphite and oxygen without UV illumination (dark) (known as the auto-oxidation reaction).

Photo-oxidation of Cerium(III)

The oxidation of cerium(III) was followed by measuring the concentration of cerium(IV) in solution using a volumetric titration method (Vogel A.I. 'A text-book of quantitative inorganic analysis' third edition, Longmans 1961, page 318). Data from the three test runs, with UV illumination and sulphite dosing, with UV illumination but without sulphite dosing, and without UV illumination but with sulphite dosing are given in Figure 10. As shown in Figure 10, unlike the case for iron(II), the auto-oxidation reaction (in the dark) was not sufficient to oxidise dissolved cerium(III). However, like iron(II), dissolved cerium(III) absorbed UV light at 254 nm and photo-initiated the oxidation reaction. The photo-oxidation reaction was clearly accelerated by the addition of 20 mg/L of sulphite per minute.

Whilst the invention has been described with reference to a number of preferred embodiments it should be appreciated that the invention can be embodied in many other forms.

CLAIMS:

1. A method for oxidising an inorganic species in an aqueous solution comprising the steps of:

- (i) supplying an oxidisable source of sulphur, and
5 oxygen to the solution; and
(ii) irradiating the solution with UV light such that the species is oxidised.

2. A method as claimed in claim 1 wherein the oxidisable source of sulphur is SO_3^{2-} , $\text{SO}_2(\text{g})$, aqueous SO_2 ,
10 HSO_3^- , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$.

3. A method as claimed in claim 1 or claim 2 wherein the inorganic species is present in the aqueous solution in trace quantities.

4. A method as claimed in any one of the preceding
15 claims wherein the inorganic species is arsenic, manganese, cerium, and/or iron.

5. A method as claimed in any one of the preceding claims wherein the wavelength of UV light is less than 300nm.

20 6. A method as claimed in any one of the preceding claims wherein dissolved oxygen is derived from air.

7. A method as claimed in any one of claims 1 to 6 wherein dissolved oxygen is derived from a gas source with an oxygen partial pressure of about 0.2 atmospheres.

25 8. A method as claimed in any one of the preceding claims wherein the aqueous solution is one of: drinking water, industrial waste water, or an industrial process liquor.

9. A method for oxidising inorganic species in an aqueous solution substantially as herein described with reference to the Examples.

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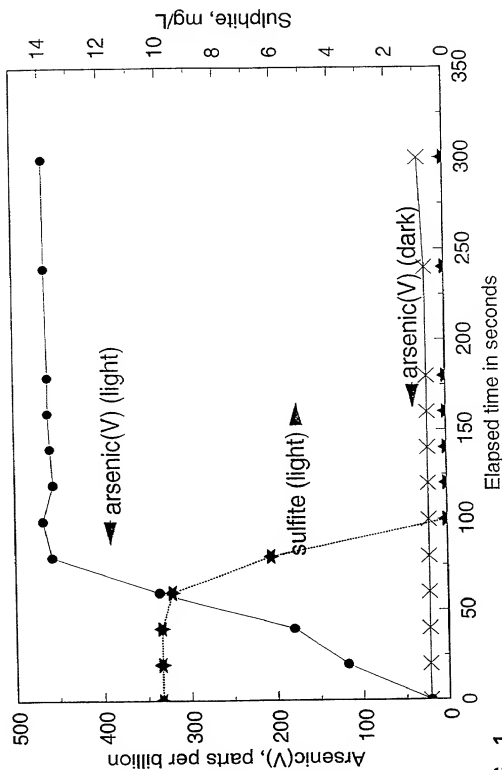


FIG. 1

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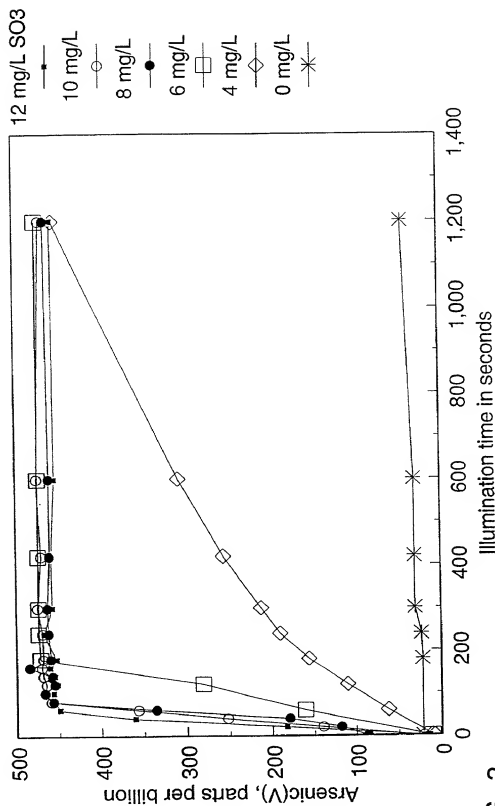


FIG. 2

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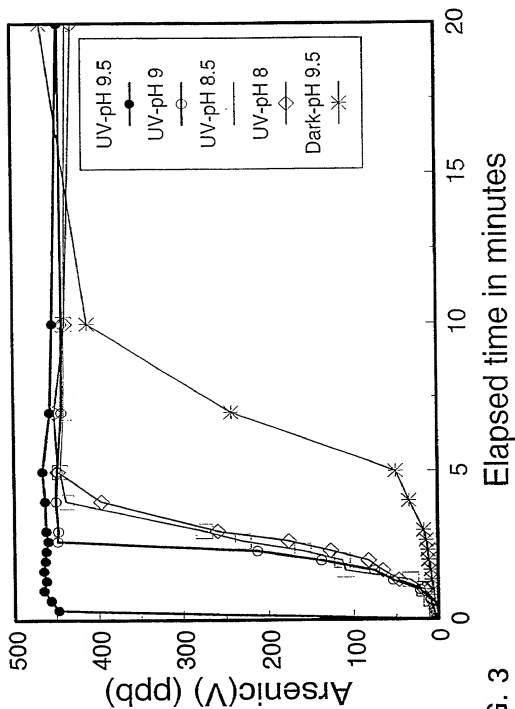


FIG. 3

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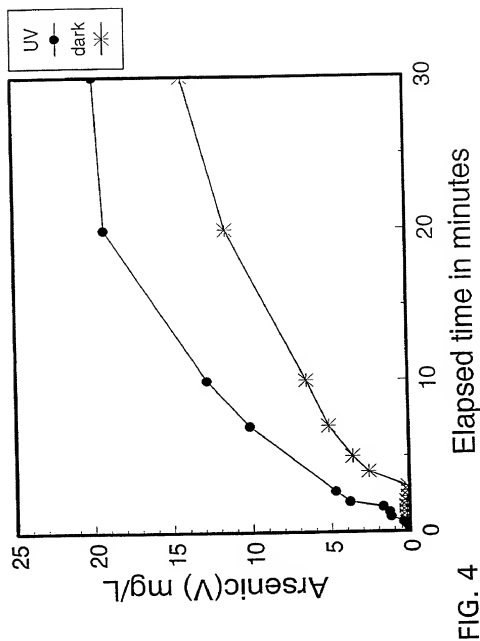


FIG. 4

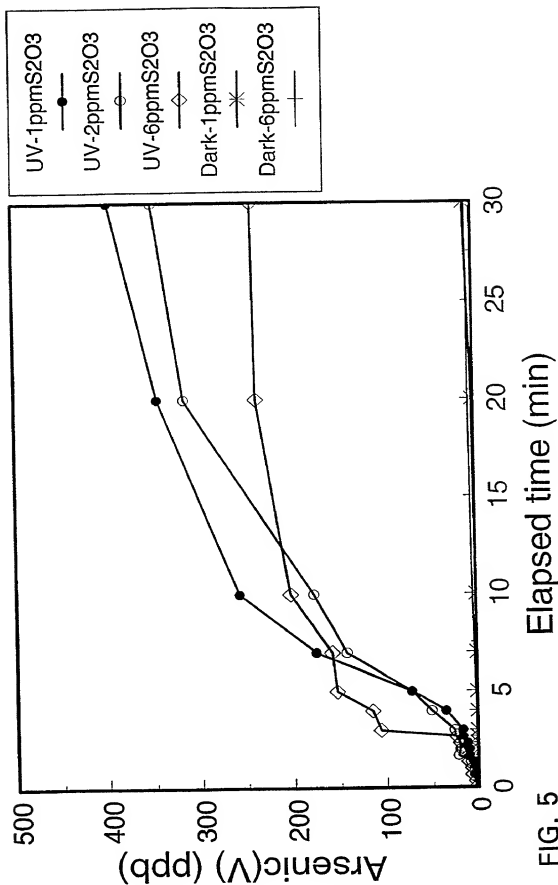


FIG. 5

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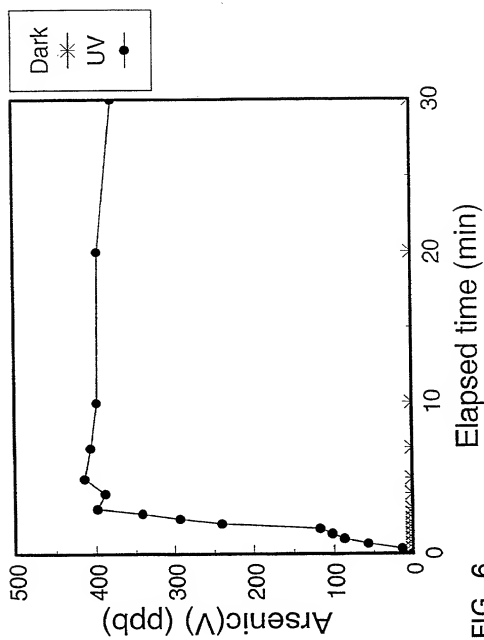


FIG. 6

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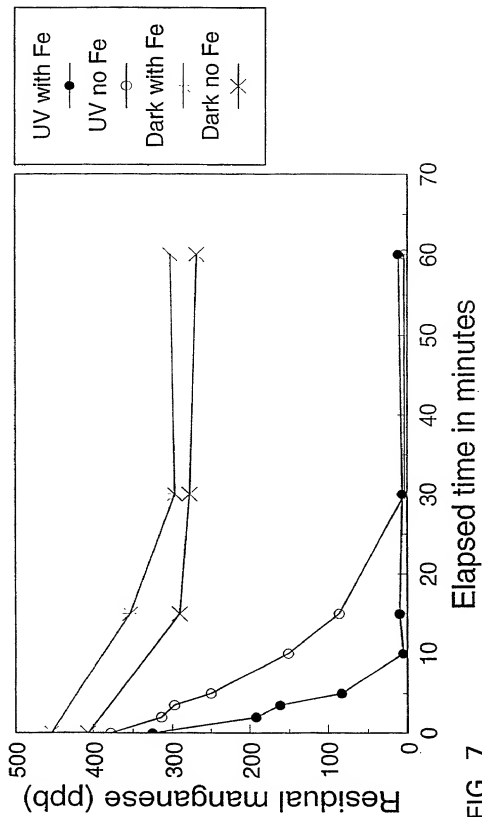


FIG. 7

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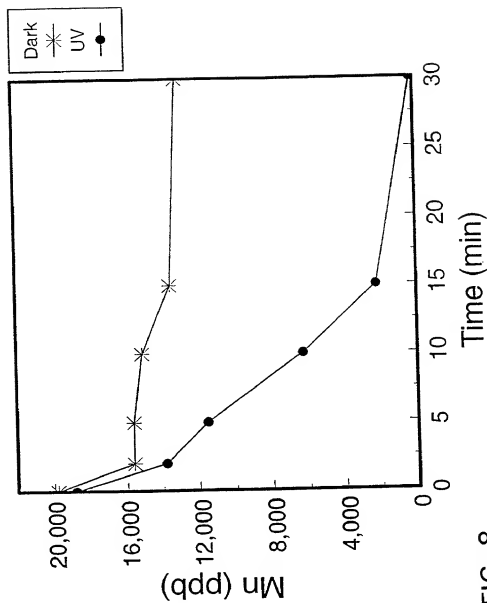


FIG. 8

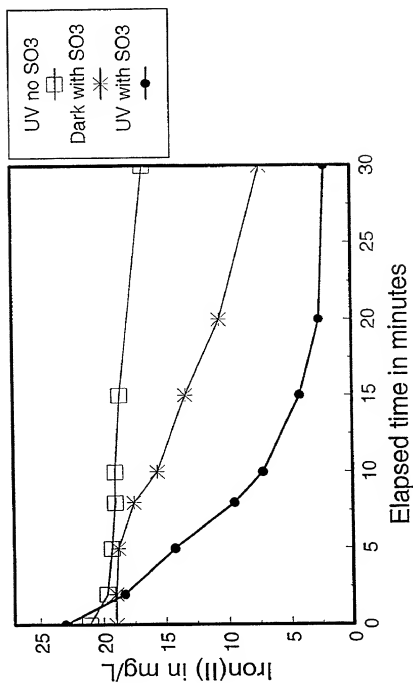


FIG. 9

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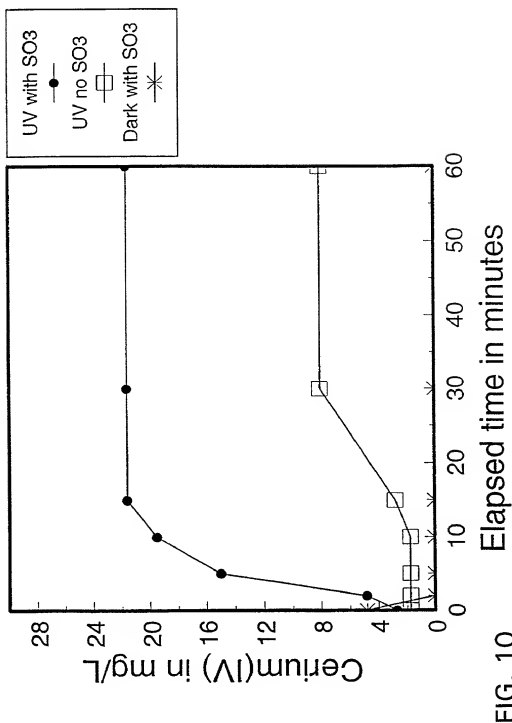


FIG. 10

COMBINED DECLARATION AND POWER OF ATTORNEY

(Original, Design, National Stage of PCT, Supplemental)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type: (check one applicable item below)

- ☐ original
☐ design
☐ supplemental
☒ National Stage of PCT
☐ divisional (see added page)
☐ continuation (see added page)
☐ continuation-in-part (see added page)

INVENTORSHIP IDENTIFICATION

My/our residence, post office address and citizenship is/are as stated below next to my/our name. I/we believe that the named inventor or inventors listed below is/are the original and first inventor or inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

 PHOTO-ASSISTED OXIDATION OF INORGANIC SPECIES IN AQUEOUS SOLUTIONS

SPECIFICATION IDENTIFICATION

The specification of which: (complete (a), (b) or (c))

- (a) ☐ is attached hereto.
 (b) ☐ was filed on with an effective filing date July 22, 1998 as
☐ Serial No. _____ or
☐ Express Mail No. _____ as Serial No. (not yet known) and was
 amended on _____ (if applicable).
 (c) ☒ was described and claimed in PCT International Application No. PCT/AU98/00576 ✓ filed on 22 July 1998 ✓ and as amended
 under PCT Article 19 on _____ (if any).

POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name(s) and registration number(s))

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 Michael J. Bujold
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Registration No. 27,868
 Registration No. 32,018
 Registration No. 42,462

☐ Attached as part of this Declaration and Power of Attorney is the authorization of the above-named attorney(s) to accept and follow instructions from my representative(s).

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(603) 624-9229

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ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I/We hereby state that I/we have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I/We acknowledge the duty to disclose to the United States Patent Office all information which is known to be material to patentability of this application as defined in § 1.56 of Title 37 of the Code of Federal Regulations.

PRIORITY CLAIM

I/We hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me/us on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

COUNTRY	APPLICATION NO.	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 37 USC 119
Australia ✓	PO 8196 ✓	23 July 1997 ✓	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

☐ I/We hereby claim the benefit, under 35 U.S.C. 119(e), of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

DECLARATION

I/We hereby declare that all statements made herein of my/our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor's signature: *Myint ZAW* Date: 27 March 2000
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